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On the Use of Grüneisen Parameters in the Treatment of Shock-Wave Data

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The relations between the thermodynamic Grüneisen parameter, γ, the parameter defined by the Mie–Grüneisen equation of state of solids, γ_e, and the average quantity $\bar{\gamma}$ involved in the energy–pressure equation which is used in the so-called reduction of shock-wave data are examined. General expressions connecting these quantities are reported, and the approximations of γ made in the reduction of shock-wave data are considered. The results of a very recent treatment of the shock-wave data for zirconium are considered. This treatment does not involve approximations of γ. The validity of the usual approximation $\gamma/V = \text{constant}$ is examined in the light of these results.

KEY WORDS: equation of state; Grüneisen parameter; shock-wave; solid-state physics.

1. INTRODUCTION

In a recent work, Barron et al. [1] reviewed the various quantities usually referred to in the literature as Grüneisen parameters or Grüneisen gammas and presented definitions using a consistent notation. The symbol γ, without subscripts, was reserved for the function usually called the "thermodynamic" Grüneisen parameter,

$$\gamma = \frac{V}{C_V}\left(\frac{\partial S}{\partial V}\right)_T = \frac{V}{C_V}\left(\frac{\partial P}{\partial T}\right)_V \tag{1}$$

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Since C_V can be expressed as $(\partial U/\partial T)_V$, one can transform Eq. (1) into

$$\gamma = V\left(\frac{\partial T}{\partial U}\right)_V \left(\frac{\partial P}{\partial T}\right)_V = V\left(\frac{\partial P}{\partial U}\right)_V \tag{2}$$

The literature concerning the applications of the γ parameter and its relations to the microscopic properties of solids is extensive, and Grimvall [2] recently reviewed the relevant aspects. It may also be mentioned that Bassett et al. [3] reported on the volume derivatives of γ in terms of measurable quantities.

Barron et al. [1] used the symbol γ_e for a closely related quantity appearing in the so-called Mie–Grüneisen equation of state of solids,

$$P(T, V) = -\left(\frac{\partial U}{\partial V}\right)_{T=0} + \frac{\gamma_e}{V}(U - U_0) \tag{3}$$

All quantities on the right-hand side must be evaluated at the volume under consideration, and U_0 denotes the value of the internal energy at 0 K. The derivation of this equation from statistical mechanics of a system of oscillators was given in the early review by Grüneisen [4] and, more recently, in the classical works by Slater [5] and Born and Huang [6]. Furthermore, Fumi and Tosi [7] examined the relation of γ_e to γ within the so-called quasiharmonic approximation of the vibrational properties of a non-metal.

A third gamma quantity has been introduced in connection with shock-wave experiments. In such experiments both P and T increase. By starting from an initial state, one can only reach states which lie on a line in the P–V–T space, the so-called Hugoniot. This line is defined by the intersection between a surface represented by the properties of the material under examination and a surface represented by the so-called Rankine–Hugoniot equation [8]

$$(P_H + P_i)(V_i - V_H) = 2(U_H - U_i) \tag{4}$$

Index i refers to the initial state, and index H to the state reached by shock-wave experiments. One is often interested in obtaining the P–V relation at room temperature from these measurements. The usual procedure, which is called reduction of shock-wave data, is based upon the estimation of the difference $P_r - P_H$ for each experimental V value, where the subscript r denotes the values at room temperature. Such estimation is performed by using what is sometimes called the energy–pressure equation [9, 10],

$$P_r - P_H = \frac{\bar{\gamma}}{V}(U_r - U_H) \tag{5}$$

where $\bar{\gamma}$ indicates an average value of the Grüneisen parameter. This equation can be derived from the definition of γ, Eq. (2), by integrating at constant volume

$$P_r - P_H = \frac{1}{V}\int_{U_H}^{U_r} \gamma \, dU \tag{6}$$

and defining the quantity $\bar{\gamma}$ as the mean value

$$\bar{\gamma} = \frac{\int_{U_H}^{U_r} \gamma \, dU}{U_r - U_H} \tag{7}$$

Since γ will, in general, be a function of V and U (or V and P), the energy–pressure equation, Eq. (5), will be exact only if such dependencies are also accounted for in the average quantity $\bar{\gamma}$, Eq. (7). However, in the usual application of Eq. (5) [9, 10], the approximation is made that γ is only a function of V. In this case Eq. (7) leads to $\bar{\gamma} = \gamma$ and the energy–pressure equation becomes

$$P_r = P_H + \frac{\gamma}{V}(U_r - U_H) \tag{8}$$

Two questions connected with Eqs. (5) and (8) motivated the present study. The first question concerns the relation between the Grüneisen gammas appearing in these equations and the quantity γ_e which is introduced in the Mie–Grüneisen formulation of the equation of state of solids, Eq. (3). This question is considered in Section 2 and the relation among the three gamma quantities is discussed. The second question concerns the use of Eq. (8). When applying this equation to the treatment of shock-wave data, two further approximations are introduced [9, 10]: (a) the volume dependence of γ is described by assuming that γ is proportional to V, and (b) the quantity $U_r - U_H$ is estimated by using Debye theory. However, it would be desirable if the shock-wave data could be treated without these approximations. In Section 3 we consider the results of a very recent [11] assessment of the thermodynamics of zirconium, where shock-wave data were treated by adopting a purely thermodynamic approach. The results of the assessment are compared with the assumptions about γ which we mentioned before. Finally, the possibility of a treatment of shock-wave data without assumptions on γ, as demonstrated here, is emphasized.

2. RELATION BETWEEN THE GAMMA QUANTITIES

2.1. Thermodynamic Derivations

We first assume that C_V and γ in Eq. (1) are known as functions of T and V. Integration under constant volume yields

$$P(T, V) - P(0, V) = \frac{1}{V}\int_0^T \gamma C_V \, dT \tag{9}$$

$P(0, V)$ can be expressed in terms of the internal energy U by applying the identity known as the thermodynamic equation of state at 0 K:

$$P = -\left(\frac{\partial F}{\partial V}\right)_T = -\left(\frac{\partial U}{\partial V}\right)_T + T\left(\frac{\partial S}{\partial V}\right)_T \tag{10}$$

$$P(0, V) = -\left(\frac{\partial U}{\partial V}\right)_{T=0} \tag{11}$$

Furthermore, since the volume is kept constant we can replace $C_V \, dT$ by dU and Eq. (9) may thus be written as

$$P(T, V) = -\left(\frac{\partial U}{\partial V}\right)_{T=0} + \frac{1}{V}\int_{U_0}^{U} \gamma \, dU \tag{12}$$

Equation (12) is identical to the Mie–Grüneisen equation of state of solids, Eq. (3), if γ_e is defined as

$$\gamma_e = \frac{\int_{U_0}^{U} \gamma \, dU}{U - U_0} \tag{13}$$

γ_e should thus be regarded as a mean value of γ over the range of U from U_0 to the actual U. In some applications it is common to assume that γ_e is a function of volume, only. Eq. (13) shows that this assumption is only an approximation unless γ is a purely volume-dependent function between U_0 and U, i.e., between 0 K and T. If that is the case, γ_e is identical to γ. If not, the approximation $\gamma_e(T, V) = \gamma(T, V)$ will overestimate the value of γ_e if γ is an increasing function from 0 K to T but underestimate the value of γ_e if γ is a decreasing function.

Finally, if information on γ_e is available, γ may be evaluated by using Eq. (13):

$$\int_{U_0}^{U} \gamma \, dU = \gamma_e(U - U_0) \tag{14}$$

$$\gamma = \left\{\frac{\partial[\gamma_e \cdot (U - U_0)]}{\partial U}\right\}_V \tag{15}$$

2.2. Consequences

Equation (7) and (13) show that $\bar{\gamma}$ and γ_e are both mean values of γ evaluated at constant volume but using different ranges of U. For $\bar{\gamma}$ one integrates from room temperature to the temperature obtained in the shock-wave experiment under consideration. For γ_e one integrates from 0 K to any temperature of interest. It is self-evident that all three, γ, $\bar{\gamma}$, and γ_e, are identical if γ is only a function of volume. Whereas this condition is exactly fulfilled by an ideal nonmetallic solid obeying the models by Einstein or Debye with volume-dependent characteristic temperatures [6], it can only be an approximation for real materials in view of the existence of anharmonic and nonvibrational contributions. In general, one should thus treat γ, $\bar{\gamma}$, and γ_e as three different quantities.

3. A THERMODYNAMIC TREATMENT OF SHOCK-WAVE DATA

In a very recent study [11], the available shock-wave data on zirconium, which were reported by McQueen et al. [10] and recently revised by Fritz [12], were treated together with information from static, low-pressure measurements by using a thermodynamic model. The model, which is discussed in Ref. 13, is based upon the so-called Murnaghan approximation [14, 15] and the use of a power series in T to describe the heat capacity at zero pressure. The result is an analytical expression involving phenomenological parameters and giving all thermodynamic properties as a function of T and P or T and V [13]. In the application of the model to Zr [11] the model parameters were evaluated from the available thermochemical and thermophysical data by using a computer optimization program [16] which allows all the various types of experimental data to be treated simultaneously. Each piece of information was given a certain weight, and the weights were changed by trial and error during the work until most of the experimental data values were satisfactorily reproduced. The set of parameter values giving the optimum description of the available information was considered as the most probable description of the system. In the evaluation of the optimum parameters describing the pressure dependence of molar volume and of the compressibility for hcp and bcc Zr, and the molar volume and expansivity of bcc Zr, information from shock-wave experiments was used. From the results of each single shock, U_H and P_H were adopted as independent variables defining the thermodynamic state of the material, and the best fit to V_H was searched for during the optimization. In particular, for bcc Zr, three parameters which describe the temperature and pressure dependence of the molar volume were evaluated in the optimization. The V_H values for hcp and bcc Zr recalculated using the optimum set of parameters for each set of experimental U_H and P_H values are compared in Fig. 1 with the input data [10, 12]. We observe that most of the experimental data points from the low-pressure range are reasonably well reproduced, but at very high pressures the experimental volume is larger than the calculated one. The phase transition shown in Fig. 1, which was detected by McQueen et al. [10], was tentatively classified in Ref. 11 as hcp to bcc, i.e., the possibility of omega Zr being involved was tentatively excluded.

The temperature of the sample undergoing a shock experiment, which is, in general, not known, is obtained from the same thermodynamic calculations reported in Fig. 1. The values obtained in Ref. 11 are shown in Fig. 2 together with the calculated hcp/bcc equilibrium boundaries. The equilibrium boundaries for omega Zr have been omitted. We observe that the material reaches indeed very high temperatures at high compressions. It should thus be interesting to examine how the changes in T and V affect

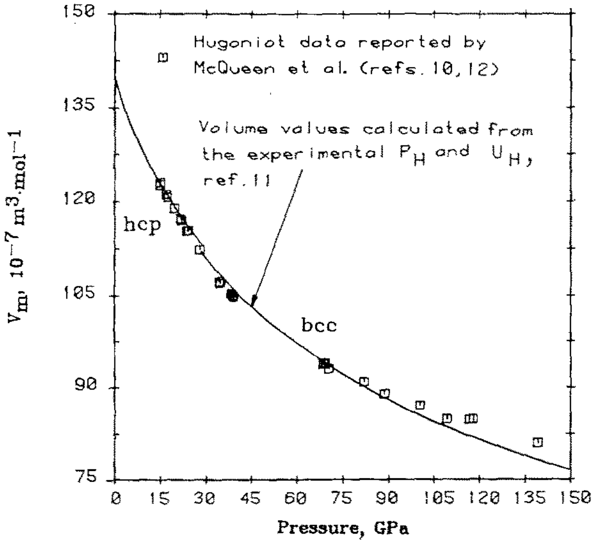

Fig. 1. The molar volume of Zr corresponding to various pressures (P_H) and values of the energy (U_H) according to the Hugoniot data obtained by McQueen et al. [10] and revised by Fritz [12], compared with the values calculated in Ref. 11. The volume value corresponding to each single shock experiment was calculated at the conditions defined by the experimental P_H and U_H using the optimum set of thermodynamic parameters assessed in Ref. 11. Lines have been drawn through the calculated points for hcp and bcc Zr.

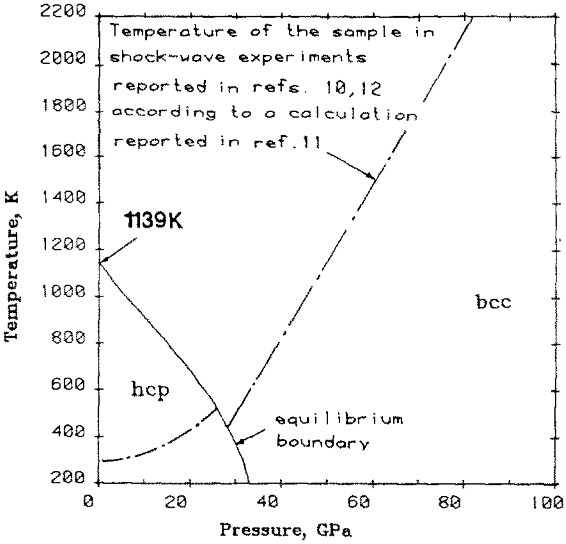

Fig. 2. The temperature of the sample in the shock-wave experiments reported by McQueen et al. [10] and revised by Fritz [12] calculated under the assumption that the formation of omega Zr is suppressed. The hcp/bcc equilibrium boundary calculated using the optimum set of thermodynamic parameters assessed in Ref. 11 is indicated. The temperature for each single shock experiment was obtained from the calculations of the volume which are shown in Fig. 1.

the Grüneisen parameter. This is demonstrated in Fig. 3 for bcc Zr, the phase which is stable up to the melting point. In Fig. 3 we report the values of γ calculated from Eq. (2) by using the optimum set of thermodynamic parameters assessed in Ref. 11 for volume values between V_r, the volume at 300 K and 101325 Pa, and 0.73 V_r and for temperatures between 300 and 2000 K. We observe that γ decreases with V at all temperatures, but the decrease is less drastic at the highest temperatures. As a consequence, the effect of temperature upon γ at a given volume is predicted by the calculation to depend upon the degree of compression. If V/V_r is higher than about 0.80, γ decreases with the increase in T, but γ increases with the increase in T if V/V_r is lower than about 0.8.

The effect of T and V upon the relation γ/V is demonstrated in Fig. 4. We observe that the ratio γ/V is not a constant but decreases with volume. However, the rate of decrease is lower at higher temperatures. An important consequence of the results shown in Fig. 4 is that the room-temperature P–V relation obtained by the use of Eq. (8) and the

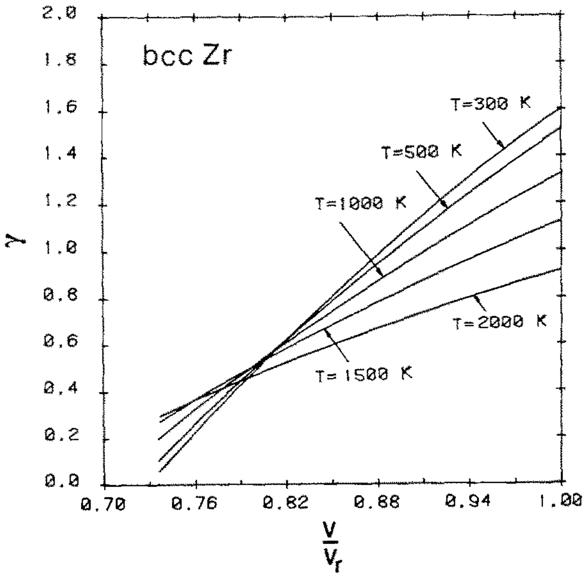

Fig. 3. The thermodynamic Grüneisen parameter for bcc Zr as a function of volume and temperature. The molar volume $V_r = 1.3839676 \times 10^{-5}\ \mathrm{m^3 \cdot mol^{-1}}$ at 300 K and 101,325 Pa [11].

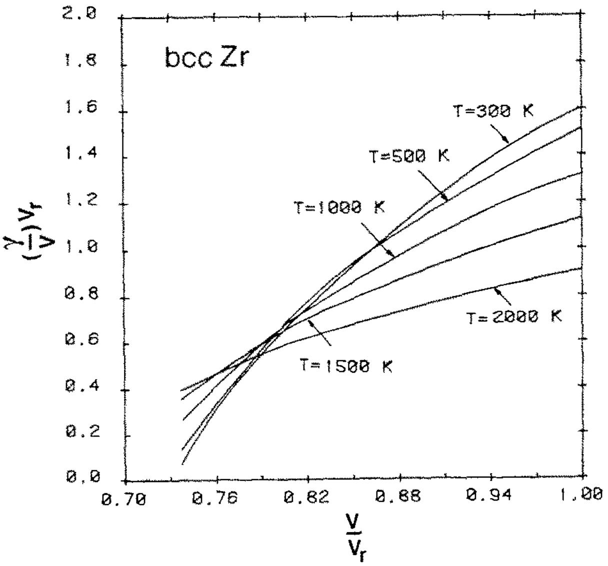

Fig. 4. The relation γ/V for bcc Zr as a function of volume and temperature. The molar volume $V_r = 1.3839676\ 10^{-5}\ \mathrm{m^3 \cdot mol^{-1}}$ at 300 K and 101,325 Pa [11].

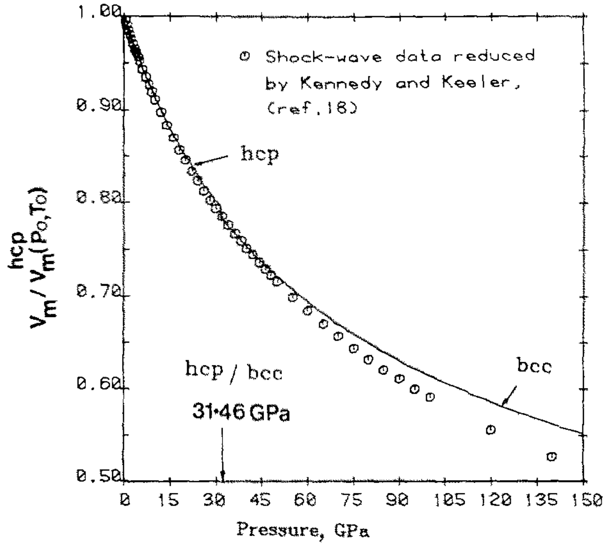

Fig. 5. The pressure dependence of the molar volume of Zr at $T_0 = 298.15$ K calculated using the optimum set of parameters assessed in Ref. 11, compared with the values obtained by Kennedy and Keeler [18] by performing a reduction of the shock-wave data compiled by VanThiel [17]. The volume values are referred to hcp Zr at $p_0 = 101{,}325$ Pa. The value 31.46 GPa is the hcp/bcc equilibrium pressure assessed according to the description from Ref. 11. The discontinuity in the assessed volume values, associated with the hcp/bcc transition is shown.

approximation $\gamma/V = \text{constant}$ may be expected to involve a certain error even in the case of the estimate of $U_r - U_H$ being accurate. In particular, if the chosen value for γ/V is close to the value from room temperature and atmospheric pressure, the magnitude of the term $(\gamma/V)(U_r - U_H)$ in Eq. (8), which is negative, might be overestimated at high compressions, i.e., the reduced value of P_r might be too low. Unfortunately, a reduction of the shock-wave data for Zr [10, 12] using all the various assumptions [9, 10] mentioned in Section 2 is not available, and thus a comparison with the P–V relation at room temperature obtained in Ref. 11 is not possible. However, shock-wave data from an earlier [17] compilation were reduced by Kennedy and Keeler [18] using a different assumption about the ratio γ/V. They treated this ratio not as a constant, but as a purely volume-dependent function, which was described using the model by Dugdale and MacDonald [19]. Their reported P–V relation at room temperature is compared in Fig. 5 with the isotherm calculated using the optimum thermodynamic parameters from Ref. 11. We observe that except for the hcp/bcc transition which is not shown by their points, the volume values from both sources are in reasonably good agreement up to about 50 GPa. At higher pressures their volume values are lower than the ones according to Ref. 11. A discrepancy between calculations and experiments but in the opposite direction was already observed in Fig. 1. However, the discrepancy shown in Fig. 5 starts at lower pressures, where the Hugoniot data [10, 12] were satisfactorily reproduced by the calculation. It may thus be suggested that the reduction procedure applied by Kennedy and Keeler seems to overestimate the magnitude of the negative term $(\gamma/V)(U_r - U_H)$ in Eq. (8), i.e., their P_r values for V/V_r ratios lower than 0.7 seem to be too low.

4. CONCLUDING REMARKS

Admittedly, the assessment of the properties of zirconium reported in Ref. 11 also based upon approximations, mainly the choice of the analytical expression for the Gibbs energy $G(T, P)$. Furthermore, it is not possible to say at present whether the strong temperature and volume dependence of the Grüneisen parameter for bcc Zr evaluated in Ref. 11 is due to peculiarities of the thermodynamics of this phase or is a feature common to the function $\gamma(T, V)$ for other transition metals. In spite of these facts, the results presented in Figs. 3 and 4 lend strong support to the suspicion that the ordinary method for reduction of shock-wave data based upon the assumption of γ being proportional to V may not be quite satisfactory. It is thus suggested that other methods of treating shock-wave data should be tested. The method applied in Ref. 11 is proposed here as a useful alternative.

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